Modifications of the C–S–H Gel by Hydration at 40°C of Belite Cements from Coal Fly Ash Class C

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The influence of the temperature on two types of hydrated fly ash belite cement (FABC) pastes were investigated at a nanoscale (1–100 nm) by measuring the specific surface area and pore-size distribution by the sorption isotherms of nitrogen gas and the BET method, and at a microscale from the pore-size distribution measured by mercury intrusion porosimetry. The two belite cements were fabricated by the hydrothermal–calcination route of fly ash class C in NaOH 1*M* solution (FABC-2-N) and demineralized water (FABC-2-W). In the case of FABC-2-W, a densification of the C–S–H gel was produced at the temperature of 40°C, which favored the formation of pores ~3 nm in diameter leading to higher surface area values, compared with the C–S–H gel formed at 20°C. At a microscale, the temperature led to an increase of capillary porosity (>0.05 μm) at a later age of hydration and, consequently, a decrease of compressive mechanical strength. In the case of FABC-2-N, the densification of the gel was less evident, but the increase of capillary porosity (pores of diameter >0.05 μm) was higher. Significant direct linear quantitative correlations were found among these nanostructure characteristics of the C–S–H gel and macrostructural engineering property such as the compressive mechanical strength, for the two FABC-2-W and FABC-2-N cements under normal conditions. At 40°C, the correlations were not so clear probably due to another microstructural factor such as the increase of the larger capillary porosity (>0.05 μm).

I. Introduction

Fly ash belite cements (FABC) have properties different from those of Portland cement, which are of considerable importance for specific applications such as the manufacture of cement-based matrices for confining radioactive liquid wastes and for dam construction, among others. FABC have a slow hydration rate so that the heat that is liberated is more gradual, and hence shrinkage problems are avoided. The hydration of FABC produces minimum amounts of $Ca(OH)_2$, and lower pH of pore solution than that of Portland cement, conditions that ensure a good durability in the aggressive atmospheres in which expansive reactions with $Ca(OH)_2$ could take place, as it is the case in the attack by sulfates, which yields considerable amount of radioactive liquid wastes.[1–6]

In this sense, we are investigating the use of FABC for the formulation of alternative matrices for confining low-level liquid wastes (LLW) and medium-level liquid wastes (MLW).[7–9] The storage of LLW and MLW in Spain is located in "The Cabril" near the city of Cordoba, where the temperature can reach values of 40°C. Thus, we were interested in studying the stability of FABC at this temperature, which is presented here.

In the case of Portland cement, there is a general consensus on the effect that the temperature has on the microstructure, porosity, and hydrated products. Skalny and Odler[10] studied, using adsorption techniques, crystalline and near-amorphous calcium silicate hydrates formed under different conditions from C_3S, β-C_2S, and synthetic tobermorite. They observed that while the surface area continuously increases with the degree of hydration at 25°C, at higher temperatures, after reaching a maximum, the surface areas per unit of nonevaporable water, W_n, decrease. The authors explained this as being due to the existence of recrystallization processes, which could lead to coarsening of the hydration products. Paul and Glasser,[11] from a study of the impact of prolonged warm (85°C) moist cure on a commercial Portland cement paste, detected a very large increase in porosity at 85°C, which arises partly as a consequence of the conversion of low-density paste constituents into higher density katoite. Cong and Kirkpatrick[12] examined the structural changes in synthetic C–S–H with a C/S ratio from 1.13 to 1.56 cured at relative humidities (rh) from 9% to 100% and temperatures from 25° to 200°C, using ^{29}Si NMR spectroscopy, XRD, and thermal analysis. They concluded that heating of C–S–H results in increasing polymerization and structural disorder, and decreased basal spacing. Thomas and colleagues,[13–15] from the study of the effect of heat treatment on the pore structure and drying shrinkage of type I Portland cement paste, concluded that heating of cement paste causes a change in the pore-size distribution, with an increase in capillary porosity and a decrease in mesoporosity due to densification of the C–S–H gel phase associated with increased polymerization of the silicates and the release of liquid water.

From the above-mentioned descriptions, it is possible to deduce that there is enough information on the influence of temperature on the microstructure and in particular on the SA, porosity, and pore-size distribution of Portland-based materials. But there is no information about the changes induced by the temperature on the hydration of belite cement and in particular the FABC.

Hence, the main aim of the present paper is to study the changes, caused by heating at 40°C for 180 days under a saturated water vapor atmosphere, of two types of FABC, called FABC-2-N (in which, a previous alkaline hydrothermal treatment of the fly ash was carried out) and FABC-2-W (in which, a previous hydrothermal treatment in demineralized water of the fly ash was carried out). The changes that resulted on the C–S–H were investigated at a nanoscale (1–100 nm) by measuring the pore-size distribution and specific surface area by means of sorption isotherms of nitrogen gas and the BET method. At a microscale, the porosity and pore-size distribution were measured by mercury intrusion porosimetry. The influence of the results on those corresponding to the mechanical compressive strength was also studied. The results were compared with those obtained at 20°C in equivalent FABC.[16,17]

II. Experimental Procedure

Spanish coal fly ash with a high Ca content (ASTM Class C), called FA-2, was used as a raw material. The chemical

Table I. Chemical Composition of the Starting Fly Ash (FA-2) and Anhydrous FABC-2-W and FABC-2-N Cements (% by Weight)

	LOI	CaO	SiO_2 (total)	Fe_2O_3 (total)	Al_2O_3	MgO	SO_3	Na_2O	K_2O	SiO_2† (reactive)	BET (m^2/g)
FA-2	4.0	32.0	32.8	4.2	19.3	2.2	2.8	0.44	1.6	25.2	3
FABC-2 W	1.4	48.3	28.7	2.3	15.2	1.4	1.7	0.25	0.5	28.6	6.4
FABC-2-N	2.7	48.3	23.6	3.0	14.4	1.2	1.2	4.5	0.38	23.5	5.5

†Silica reactive according to Spanish standard UNE-80-224. FABC, fly ash belite cement; LOI, loss on ignition.

composition of the starting fly ash and cements (Table I) was determined according to the Spanish standard UNE-EN 196-2.

The fabrication process of the FABC, called FABC-2, involved two steps. A mixture of FA-2 and commercial CaO at a Ca/Si molar ratio of 2 was firstly hydrothermally treated in 1*M* NaOH solution (or demineralized water) at a solution-to-solid ratio of 3:1 for 4 h at a temperature of 200°C with continuous stirring and 1.24 MPa pressure. The solid obtained after filtration was washed three times with demineralized water to eliminate excess NaOH. In a further step, the dried solid (80°C overnight) was heated at a rate of 10°C/min up to 600°C and at 5°C/min from 600° to 800°C. The chemical compositions of the two cements, called FABC-2-N and FABC-2-W for NaOH 1*M* solution and demineralized water, respectively, are given in Table I. More characterization details can be found in reference.[9]

Pastes were prepared at a demineralized water-to-cement ratio of 0.82 and 0.68 for FABC-2-N and FABC-2-W, respectively, with a commercial water reducer additive (Rheobuild-1000, Degussa Construction Chemicals, Barcelona, Spain) in a proportion of 2% (by weight of cement). After mixing, a series of six prisms were molded into 1 cm × 1 cm × 6 cm specimens and compacted by vibration. The samples were demolded after 1 day at >95% rh and cured at 40°C under >95% rh in sealed containers for a period ranging from 1 to 180 days from mixing.

The compressive mechanical strength was measured in every series of six samples. Then, a part of the samples were cut into monolithic pieces about 7 mm in size. The gel characterization at a nanoscale (1–100 nm) was evaluated from the BET surface area and pore-size distribution analysis. Monolithic pieces of about 7 mm size were previously dried at room temperature in desiccators with silica gel, up to a constant weight, to eliminate free water (evaporable water), and then about 0.5 g of sample was degasified at 50°C (to prevent decomposition of C–S–H gel) under vacuum up to 5 μm Hg pressure.

The hydrothermal treatment was carried out with a Parr (PARR Instrument Company, Illinois, USA) model 4522 (a 1000 mL pump with a split-ring closure and a PID model 4842 temperature controller, Parr Instrument Co.). XRD patterns were recorded on a Philips (Eindhoven, the Netherlands) PW 1730 diffractometer with Cu$K\alpha_1$ radiation. Surface-area measurements were made by the BET multipoint method (Model ASAP 2010, Micromeritics Instrument Corp., Norcross, GA) using N_2-77 K gas. The surface areas were calculated from the sorption isotherm data, using the BET method,[18] in the relative pressure range of 0.003–0.3. Pore volume and pore-size distributions were calculated according to the Barret–Joyner–Halenda method,[19] using data from the adsorption isotherm branch. The porosity and pore-size distribution were investigated by mercury intrusion porosimetry carried out with a Micromeritics (Micromeritics Instrument Corp., Norcross, GA) Pore Sizer IV 9600 V1.05, in the pressure range of 0.5–33 000 psia. SEM analysis was performed with a JEOL (Tokyo, Japan) 5400 instrument equipped with an energy-dispersive X-ray spectroscopy module (EDS) Oxford ISIS model (Oxford University, Oxford, UK). The samples were covered with carbon by sput-

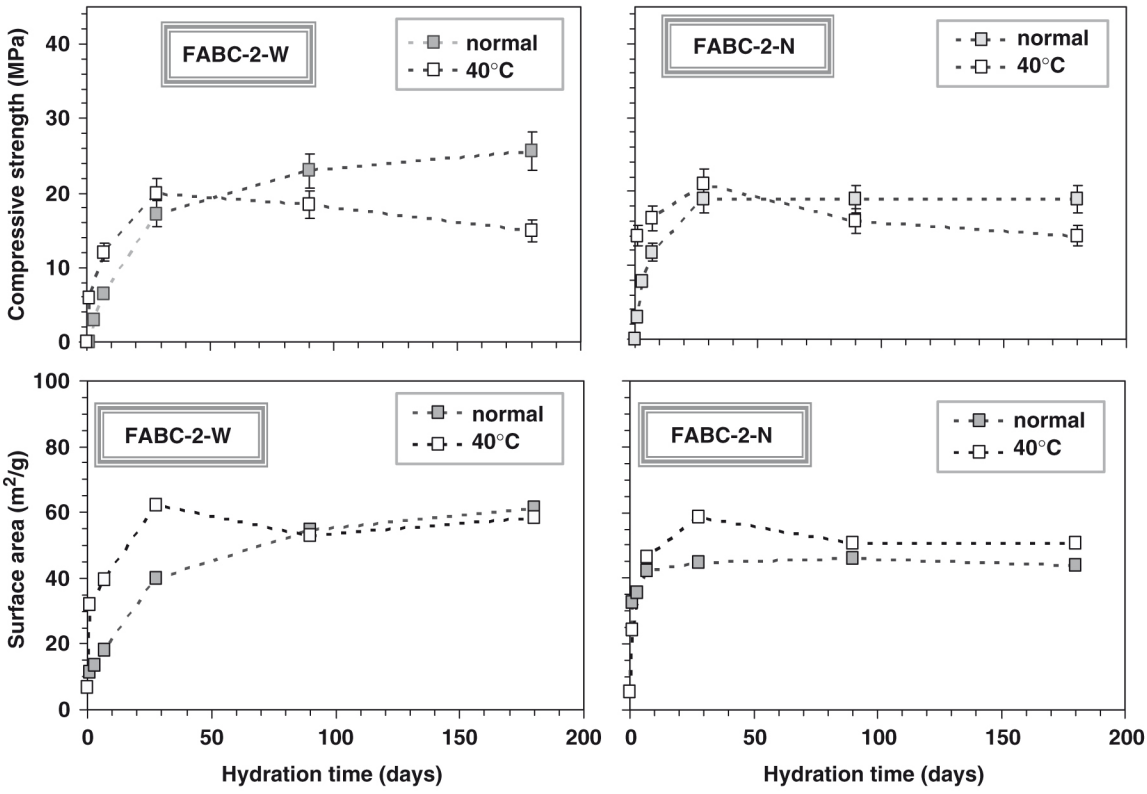

Fig. 1. Change of compressive strength and surface area with hydration time of FABC-2-W and FABC-2-N pastes: influence of the curing temperature. FABC, fly ash belite cement.

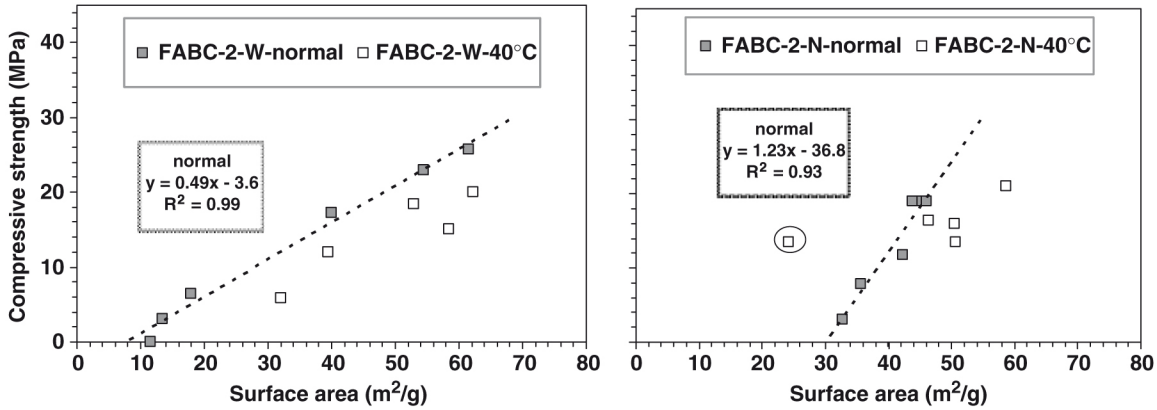

Fig. 2. Quantitative correlations between compressive strength and surface area.

tering. SEM/EDX semiquantitative analyses were performed at an accelerating voltage of 20 kV and a reference current of 300 μA on powder samples to determine the alkaline, alkaline-earth: iron oxide, alumina, silica, and sulfur contents. EDX microanalysis was carried out in the spot mode over each different crystalline phase, the limit detection being 0.2%.

III. Results

(1) Surface Area and Mechanical Strength

For normal curing, the evolution with time of compressive strength and surface area is similar and adjusted to a direct logarithmic function for the two FABC-2-W and FABC-2-N cements (Fig. 1). The temperature of 40°C increased, at early ages of hydration, the gain rate of both the compressive mechanical strength and the surface area, which were markedly higher than those obtained at normal curing. Nevertheless, the temperature of 40°C led to a decrease of both the compressive mechanical strength and the surface area after 28 days of hydration.

The main difference between the two belite cements was the hydration rate, which was faster at early ages, in the case of FABC-2-N in comparison with that of FABC-2-W. This deduction was made from the higher values of the two parameters measured.

Given that the major contribution to the surface area is due to the C–S–H gel and that it is responsible for the mechanical properties, quantitative correlations are expected to be found among them, as can be seen in Fig. 2, where a direct linear regression is obtained for normal curing. The slope is markedly higher in the case of FABC-2-N. When the curing was carried out at 40°C, the points are located, in general, to the right of the line, indicating higher surface area values for a given compressive strength, or a lower compressive strength for a given surface area value.

These quantitative correlations are very useful tools for the prediction of the mechanical behavior of new materials such as the FABC studied here, and to validate the nanostructural data obtained from adsorption isotherms of N_2-77, which are directly related to C–S–H gel development.

(2) Pore-Size Distribution from Sorption Isotherms

To explain and understand the changes induced by the temperature on the C–S–H gel, its pore-size distribution was measured at a nanoscale (1–100 nm) from the adsorption of N_2 gas after 180 days of hydration. In general, two ranges of pore sizes are well defined by the peaks centered at about 3 and 12 nm diameters (Fig. 3). As can be seen, the temperature influences the C–S–H pore-size distribution; at 40°C, the intensity of the peak centered at 12 nm decreased as that of the peak centered at 3 nm increased. This behavior indicated a refinement of the C–S–H gel pores.

IV. Discussion

The decrease of the mechanical compressive strength in both belite cements (FABC-2-W and FABC-2-N) caused at the temperature of 40°C is in apparent contradiction with the refinement of the C–S–H gel pore structure shown in Fig. 3.

This behavior is also supported by the results of Thomas and Jennings[13] on hydrated type I Portland cement cured at 60°C.

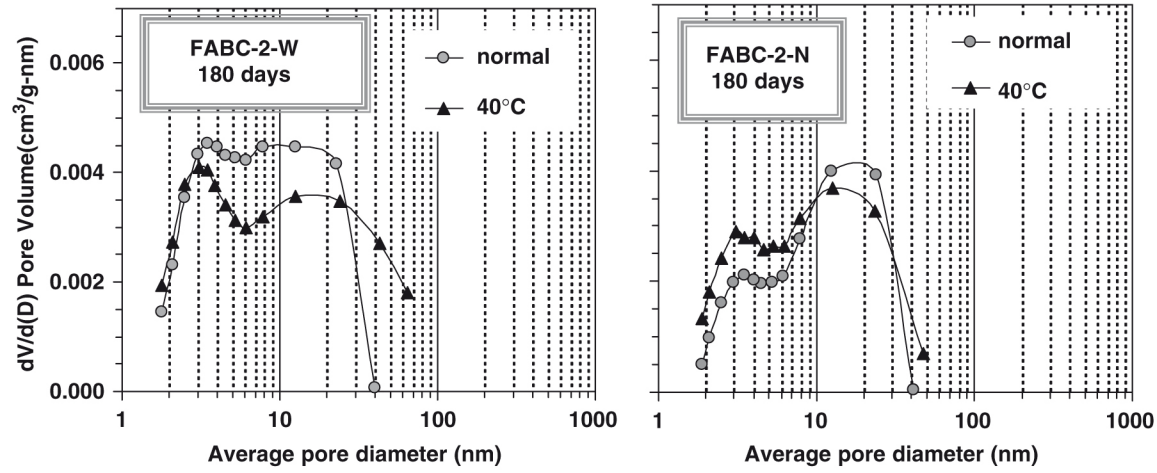

Fig. 3. Pore-size distribution curves obtained from nitrogen adsorption of FABC-2-W and FABC-N pastes: influence of curing temperature. FABC, fly ash belite cement.

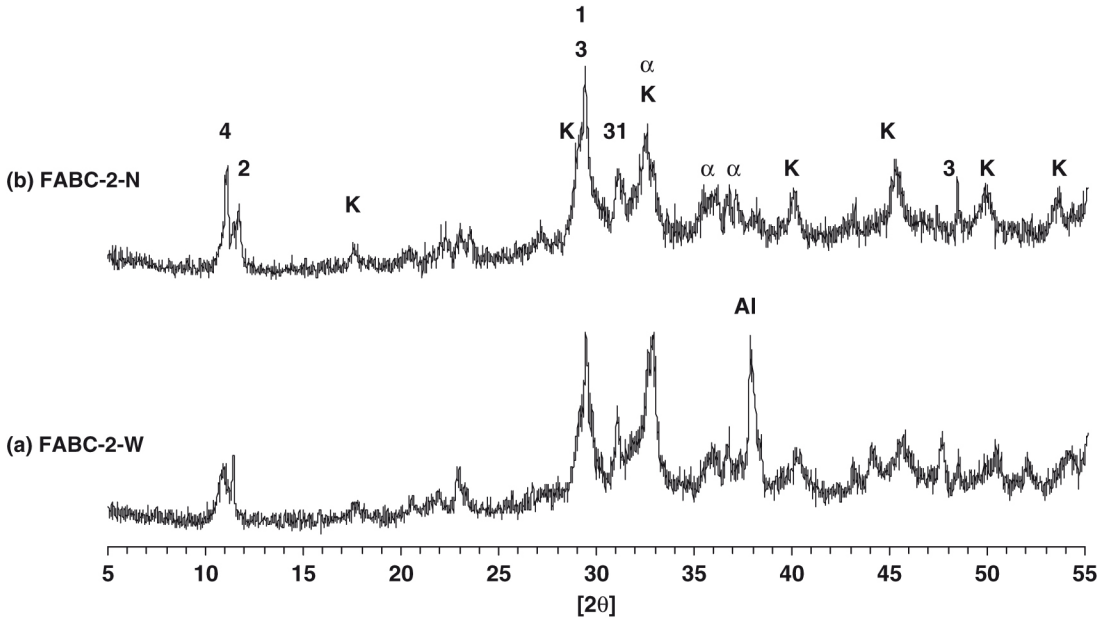

Fig. 4. X-ray diffraction patterns of fly ash belite cement pastes hydrated for 180 days at 40°C.

The authors, on the basis of a previous work,[12] explained that the temperature led to an increase in the degree of polymerization in the C–S–H gel according to oxolation reactions and liberation of one water molecule:

$$-\mathrm{Si}-\mathrm{OH} + \mathrm{HO}-\mathrm{Si}- \rightarrow -\mathrm{Si}-\mathrm{O}-\mathrm{Si}- + \mathrm{H_2O} \qquad (1)$$

The loss of water increased the C–S–H density, also being responsible for the increase of larger capillary pores. If this is true, in our case, the increase of larger capillary pores could justify the loss of compressive strength of Fig. 1.

As Paul and Glasser[11] stated, another effect caused by the temperature, which could increase the amount of larger capillary pores, is the conversion of low-density paste constituents into a higher-density katoite ($Ca_3(Al,Fe)_2\ (SiO_4)_{3-x}\ (OH)_{4x}$), which is not normally found at 25°C. This was also found in the case of FABC, as can be seen in Fig. 4, where a cubic katoite ($Ca_3Al_2(SiO_4)(OH)_8$) is formed in both pastes but with a higher intensity in the case of the FABC-2-N.

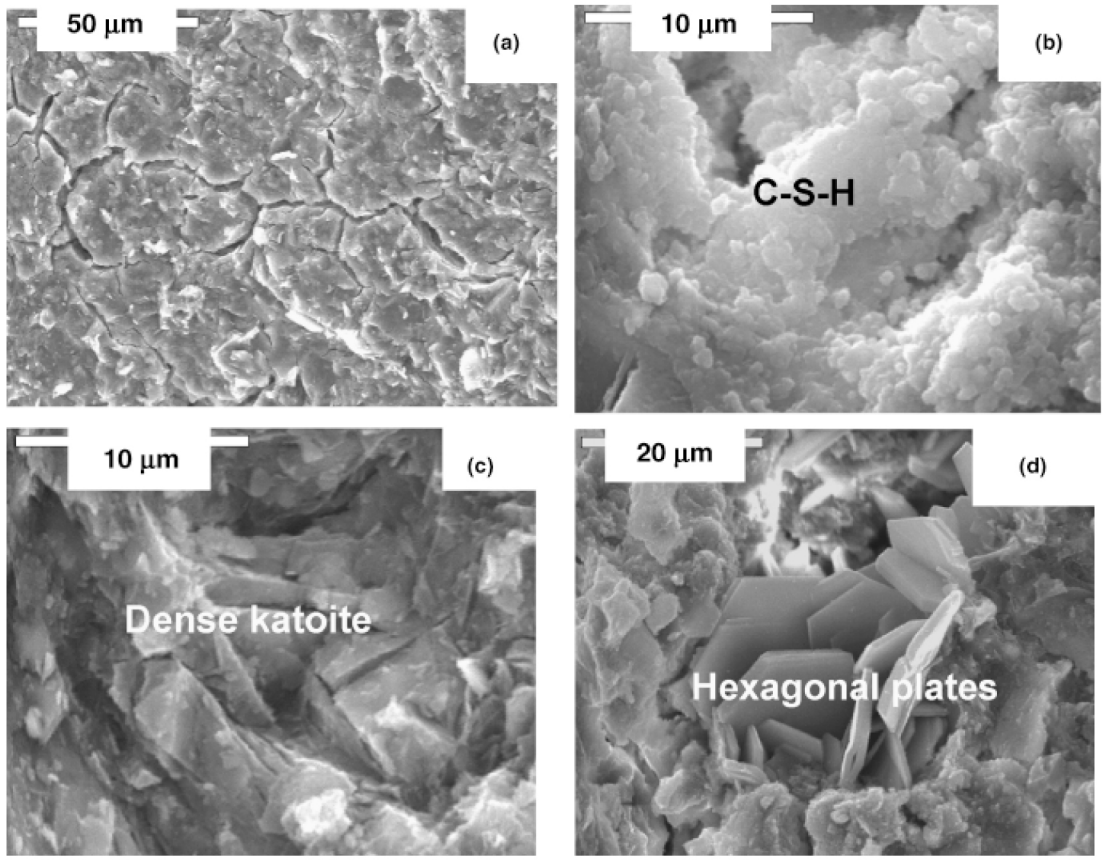

Fig. 5. Scanning electron microscopic images of hydrated FABC-2-N pastes at 40°C for 180 days. FABC, fly ash belite cement.

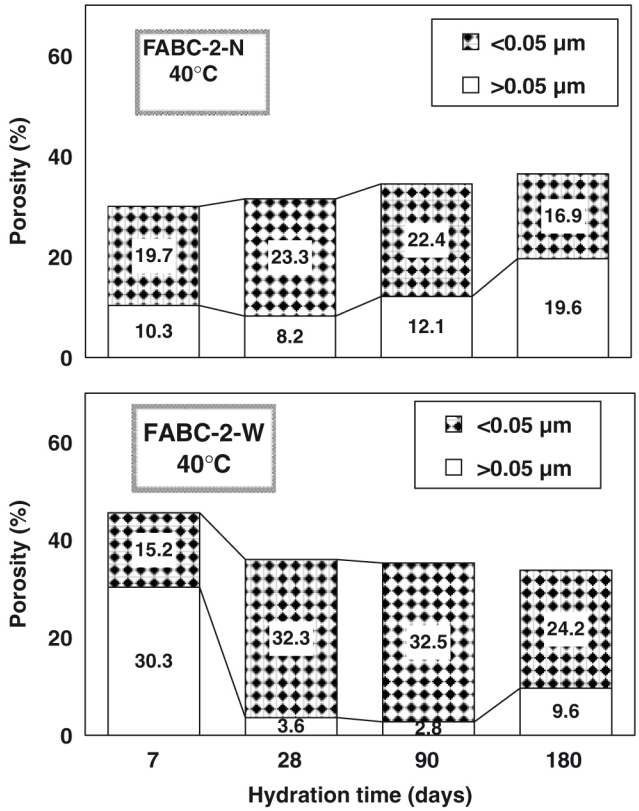

Fig. 6. Quantitative evolution of pores of diameter >0.05 and <0.05 μm of FABC-2-W and FABC-2-N pastes cured at 40°C (determined by mercury intrusion porosimetry). FABC, fly ash belite cement.

Between 10 and 12 of the 2θ angular zone, two reflections appeared that correspond the first to the basal space of hydrated calcium-monosulfo-aluminate ($[Ca_2Al(OH)_6H_2O]_2SO_4 \cdot 8H_2O$), which shifted to higher values perhaps due to carbonation and formation of the hydrated calcium-monocarbo-aluminate ($[Ca_2Al(OH)_6H_2O]_2CO_3 \cdot 9H_2O$), both of the hexagonal lamellar AFm structural family.[20]

Besides, Paul and Glasser[11] observed that the composition of the C–S–H gel changed with temperature: the Si/Ca molar ratio increased from 0.58 at 25°C to 0.66 at 85°C (if only Ca and Si are considered). This decreasing ratio effectively liberates calcium, which is incorporated into other phases, mainly katoite. In our case, a very similar Si/Ca atom ratio was obtained for the C–S–H gel of FABC-2-W (0.57 at 20°C and 0.69 at 40°C), and, therefore, one can expect that the liberated Ca is incorporated into the katoite. The aspect of dense katoite zones, hexagonal plates together with C–S–H, and microcracks formed in the dried paste, which could increase the larger capillary pores, can be seen in Fig. 5. The microcracks could be formed by the shrinkage due to the exhaustive drying of samples during its preparation for examination in the microscope and for obtaining gas adsorption–desorption isotherms.

Given that both mechanisms, the formation of katoite and polymerization of C–S–H gel as well as the cracks, converge in the formation of larger capillary pores, we decided to measure this type of pores by mercury intrusion porosimetry.

As can be seen in Fig. 6, in the case of the FABC-2-W paste, the total porosity decreased with hydration time from 46% after 7 days to 34% (by weight) after 180 days; more relevant changes were found in the pore-size distribution, where the amount of pores of diameter >0.05 μm strongly decreased with hydration time (from 30.3% to 2.8% after 7 and 90 days, respectively), whereas the amount of pores of diameter <0.05 μm strongly increased (from 15.2% to 32.5% after 7 and 90 days, respectively). From 90 to 180 days, the behavior is opposite: an increase of larger pores was found (from 2.8% to 9.6%), whereas the amount of pores of diameter <0.05 μm decreased (from 32.5% to 24.2%).

The porosity of FABC-2-N pastes is markedly lower at early ages, compared with that of FABC-2-W (30% vs 46% after 7 days), but from 28 days of hydration, the number of larger pores (>0.05 μm) is considerably higher. The percentage of these pores increased over time from 8.2% to 19.6% as those corresponding to diameter lower than 0.05 μm decreased from 23.3% to 16.9%, justifying the loss of mechanical strength.

V. Conclusions

(1) Parallel evolution of compressive strength and surface area with hydration time is found at early ages of hydration for the two FABC-2-W and FABC-2-N belite cements.

(2) The temperature of 40°C yielded, at early ages, compressive mechanical strength and surface area values markedly higher than those obtained at 20°C; nevertheless, at a later age of hydration the temperature led to a decrease of the compressive mechanical strength, but not for the surface area.

(3) In the case of FABC-2-W, a densification of the C–S–H gel was found at the temperature of 40°C, which favored the formation of pores ~3 nm in diameter leading to higher surface area values, compared with the C–S–H gel formed at 20°C. In the case of FABC-2-N, the densification of the gel was less evident. Nevertheless, the temperature of 40°C led to an increase of capillary porosity (>0.05 μm) at a later age of hydration and, consequently, a decrease of compressive mechanical strength.

(4) The temperature of 40°C favored the formation of more dense cubic katoite (Ca_3Al_2 $(SiO_4)(OH)_8$) at later ages of hydration, which is more evident for the FABC-2-N.

(5) Significant direct linear quantitative correlations were found among the nanostructure characteristics of the C–S–H gel and macro structural engineering property such as the compressive mechanical strength for the two FABC-2-W and FABC-2-N cements under normal conditions. At 40°C, the correlations were not so clear probably due to another microstructural factor such as the increase of larger capillary porosity (>0.05 μm) and formation of cracks.

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